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(21) International Application Number: PCT/GB99/02978 (22) International Filing Date: 8 September 1999 (08.09.99) (30) Priority Data: 9819600.9 8 September 1998 (08.09.98) GB (71) Applicant (for all designated States except US): A.H. MARKS AND COMPANY LIMITED [GB/GB]; Wyke Lane, Wyke, Bradford, West Yorkshire BD12 9EJ (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): BUSHBY, Richard [GB/GB]; School of Chemistry, University of Leeds, Leeds LS2 9JT (GB). LORD, Nigel [GB/GB]; School of Chemistry, University of Leeds, Leeds LS2 9JT (GB). (74) Agent: JONES, Alan, John; Carpmaels & Ransford, 43 Bloomsbury Square, London WC1A 2RA (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: CHEMICAL COMPOSITIONS (57) Abstract A composition comprising: an effective amount sufficient to inhibit polymerisation of an ethylenically unsaturated monomer or mixture of monomers polymerisable by free radical polymerisation of at least one compound which is capable of acting as a reducing agent ("Component 1") and at least one metal-containing compound where the metal is capable of existing in an ionic form with at least two different oxidation states ("Component 2") and optionally at least one compound capable of acting as a proton acid ("Component 3"), said composition comprising (i) 30 to 99.9 % by weight of Component 1 based on the total weight of Components 1 and 2 and 3; (ii) 0.1 to 25 % by weight of Component 2 based on the total weight of Components 1 and 2 and 3; and (iii) 0 to 69.9 % by weight of Component 3 based on the total weight of Components 1 and 2 and 3; and the use thereof as a free radical capture agent or scavenger, particularly for inhibiting polymerisation of an olefinic compound during distillation or purification or storage.		

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CHEMICAL COMPOSITIONS

This invention relates to free radical capture agents or scavengers and in particular to free radical capture agents or scavengers for use as or in connection with inhibitors of
5 olefinic polymerisation or of oxidative degradation (whether induced by exposure to heat or light or otherwise) of organic materials and the like.

The present invention will be described below with particular reference to inhibition of olefinic polymerisation, but is not to be construed as being limited thereto.

10

It is well known that olefinic compounds such as styrene, butadiene, acrylic monomers have a strong tendency to polymerise when subjected to prolonged storage or when heated. It is common practice to use high temperature techniques such as distillation during the separation and purification processes employed in the industrial production of
15 these olefinic compounds.

It is well established that the polymerisation of these olefinic compounds is initiated and propagated by mechanisms which involve free radicals (see for example Mechanism and Kinetics of Addition Polymerisation by M Kucera, (1992), published by Academia
20 Praha, pages 75 to 79).

Similarly it is known to use free radical scavengers to prevent the oxidative degradation of organic materials which occurs particularly on exposure to light (see for example "Plastic Additives" by Gächter and Muller, published by Oxford University Press, 4th
25 Edition, Pages 190-195). Many organic polymers particularly plastics and surface coatings are susceptible to this degradation which involves the action of free radicals.

Although it is established that there is a general utility in employing free radical capture agents or scavengers to inhibit or retard olefinic polymerisation or oxidative degradation
30 of organic materials, there remains a requirement for higher efficiency free radical scavengers which are capable of providing the desired effects at lower dosage levels or alternatively which provide a greater degree of the desired effects at the same dosage levels currently employed. There also remains a requirement that materials employed for these purposes are available in quantities and at prices which enable their ready

acceptance into the utilising technologies. Advantages accruing from using lower dosage levels include financial economy and reduced toxicity and environmental effects. Advantages accruing from a greater degree of the desired effect include financial economies arising from reduced wastage and/or prolongation of the active life of the
5 subject matter which is being protected.

The present invention is exemplified with reference to utility in inhibition of olefinic polymerisation but is not limited thereto and has the full applicability referred to above. In order to prevent or reduce the undesired polymerisation of olefinic compounds during
10 high temperature processes various compounds and compositions have been used as free radical scavengers. These polymerisation inhibitors have had varying degrees of success.

In a typical process involving an olefinic compound it is contacted with the
15 polymerisation inhibitor before being subjected to processing for example before being distilled. There remains however a significant problem. In some cases the amount of polymer formed during such processing is substantially higher than desired and this causes economic loss. In other cases it may be possible to achieve economically desirable low levels of polymerisation but only by using quantities of polymerisation
20 inhibitor which themselves are economically unacceptable. There is therefore a requirement for a cost-effective polymerisation inhibitor.

Polymerisation inhibitors have been used for many years. Sulphur was widely employed but because of difficulties in handling and disposal it has been largely replaced by non-
25 sulphur inhibitors (NSIs).

A number of different NSIs has been disclosed.

The performance of these various NSIs can be classified into two groups.
30

Firstly, there are NSIs which reduce the rate and/or the extent of polymerisation which occurs but do not eliminate it. These NSIs are termed 'retarders' and include various phenols, nitrophenols etc as described in a large number of references, for example: Plant Oper Prog 7 (4), pages 270-4 (1988) or US 4,466,904; US 4,341,600 and US

4,252,615. Although a retarder does not eliminate polymerisation it is often the case that the polymerisation is reduced to a conveniently low level. In other situations even lower levels or even complete absence of polymerisation may be required and this is not attainable using a retarder.

5

Where a retarder does not afford sufficient control of polymerisation it is necessary to employ an NSI from the second group which may be referred to as "true inhibitors". When a true inhibitor is present under the appropriate conditions essentially no polymerisation is observed. This is because the free radical capture or scavenging activity of the true inhibitor is sufficiently high to substantially eliminate the possibility of free radical initiation or propagation of polymerisation. The known range of true inhibitors includes stable free radicals. For example in "Mechanism of Polymer Reactions" by G M Burnett, Interscience, New York, 1954 (page 76), it is stated that a sterically hindered nitroxyl radical (2,2,6,6-tetramethyl-piperidiny-1-oxyl radical referred to as TEMPO) is effective against carbon centred radicals. The use of stable free radicals as scavengers was reviewed in "Free Nitroxyl Radicals" by E G Rozantsev, (1970), published by Plenum Press, Page 105 et seq. The practical utility of nitroxyl radicals as radical scavengers to prevent polymerisation was disclosed in UK Patents 1,127,127 and 1,218,456. However the high cost of stable free radicals has restricted their commercial use and there remains a requirement for an economic true inhibitor as a means of preventing or controlling polymerisation. It was further disclosed in US 4,670,131 that certain stable free radicals are capable of being used effectively under certain conditions as polymerisation inhibitors where economic levels of less than 700 parts per billion are employed. However such low usage rates are not of general applicability and there still remains a requirement for an economic means of preventing or controlling polymerisation under commonly experienced conditions.

We have now found that a composition which includes a redox agent in combination with a metal containing compound and an optional additional proton source compound has the necessary free radical capture or scavenging properties to be a true inhibitor without the economic disadvantages of the previously described compositions.

Accordingly, the present invention provides a composition comprising an effective amount sufficient to inhibit polymerisation of an ethylenically unsaturated monomer or mixture of monomers polymerisable by free radical polymerisation of:

at least one compound which is capable of acting as a reducing agent ("Component 1");

5 at least one metal-containing compound where the metal is capable of existing in an ionic form with at least two different oxidation states ("Component 2"); and

optionally at least one compound capable of acting as a proton acid ("Component 3"), said composition comprising

- 10 (i) 30 to 99.9% by weight of Component 1 based on the total weight of Components 1 and 2 and 3;
- (ii) 0.1 to 25% by weight of Component 2 based on the total weight of Components 1 and 2 and 3; and
- (iii) 0 to 69.9% by weight of Component 3 based on the total weight of Components 1 and 2 and 3,

15 wherein the ingredients amount to a total of 100%.

Compounds of Component 1 may be selected from the group comprising organic compounds characterised in that they possess an electrode potential relative to the standard silver/silver chloride electrode in acetonitrile in the range 0.00V to +1.2V and
20 preferably in the range 0.50V to +0.9V.

Compounds of Component 2 may be selected from the group comprising metal containing compounds, including organometallic compounds, which are soluble in or miscible with the material to be protected.

25

Compounds of Component 3 may be selected from the group comprising organic acids preferably with a pKa in the range 0.5 to 12 which group includes optionally substituted aliphatic branched or straight chain carboxylic acids containing up to 22 atoms, aromatic carboxylic acids and heterocyclic carboxylic acids, optionally substituted phenols and
30 alcohols.

Examples of preferred compounds of Component 1 include phenylpyrazolidones such as 1-phenyl-3-pyrazolidone (phenidone A) and 4-methyl-1-phenyl-3-pyrazolidone (phenidone B), amino-substituted aromatic compounds such as 4-aminophenol and 1,8-

diaminonaphthalene, 4-hydroxycoumarin, anthracene, phenothiazine and hydroxylamine compounds including dialkyl, alkyl aryl, diaryl and cycloaliphatic hydroxylamines, such as N-hydroxypiperidines.

- 5 Examples of suitable metal containing compounds of Component 2 include metal carboxylate salts such as cobalt versatate and copper naphthenate, and organometallic complexes such as ferrocene, ruthenocene and 1,1'-diferrocenylethylene.

It is also provided that the individual characteristic features of Components 1, 2 and 3
10 may be in individual chemical compounds or two or more of these characteristic features may be in one chemical compound.

The composition may be used as a free radical capture agent or scavenger composition. In particular, the composition may be used for inhibiting polymerisation of an olefinic
15 compound during distillation or purification or storage.

The present invention in a further aspect provides a process for inhibiting the premature polymerisation of an olefinic compound during distillation or purification which comprises incorporating therein an effective inhibiting amount sufficient to prevent
20 premature polymerisation during distillation or purification of said olefinic compound, of a mixture of:

- (i) 30 to 99.9% by weight of Component 1 based on the total weight of Components 1 and 2 and 3;
- (ii) 0.1 to 25% by weight of Component 2 based on the total weight of Components
25 1 and 2 and 3; and
- (iii) 0 to 69.9% by weight of Component 3 based on the total weight of Components 1 and 2 and 3,

wherein the ingredients amount to a total of 100%.

- 30 The olefinic compound stabilisation achieved by the present invention in using a combination of a reducing agent (Component 1) with a metal containing compound (Component 2) is particularly unexpected since in the absence of the reducing agent (Component 1) it has been known for such metal containing compounds (Component 2) to be without any activity as inhibitors or retarders of olefinic polymerisation and even to

have the entirely opposite effect in that such metal containing compounds (Component 2) often actually act as polymerisation promoting agents for olefinic compounds.

Furthermore, the olefinic compound stabilisation achieved by the present invention in using a combination of a reducing agent (Component 1) with a metal containing compound (Component 2) may be enhanced to an unexpected degree by the presence of a proton acid compound (Component 3). This effect of proton acid compound (Component 3) in the compositions of the present invention is particularly unexpected since in the absence of the other Components proton acid compounds (Component 3) may show no useful activity either as true inhibitors or retarders of olefinic polymerisation.

The effective amount of true inhibitor composition according to the present invention may vary over a wide range depending upon the particular olefinic compound involved and the distillation and purification conditions employed. Preferably the total amount of Component 1 plus Component 2 plus optional Component 3 is from about 700 ppb to about 2000 ppm based upon the weight of the olefinic compound being stabilised. For most olefinic compounds the total amount of the Components 1 and 2 and 3 is preferably in the range 5 to 1000 ppm. As the temperature increases greater amounts of true inhibitor are required. During distillation of olefinic mixtures the temperature of the reboiler is up to about 150°C. Since the boiling points of the various compounds of Components 1, 2 and 3 are different, compounds which have the desired boiling points are selected. The compositions of this invention which inhibit the polymerisation of the olefinic compound are also well suited for protecting the re-boiler sections of a distillation column during distillation of olefinic compounds or the compressor sections before entering a distillation column. The polymerisation inhibitor composition can be introduced into the olefinic compound to be protected by any conventional method. It may for example be added as a concentrated solution in a suitable solvent. Since the solubilities of the components of the compositions of the present invention are different, compounds which have the desired solubilities may be selected. In addition the components may be injected separately into the distillation train along with the incoming feed, or through separate entry points providing there is an efficient distribution of the inhibitors. Since the inhibitors are gradually depleted during the distillation operation, it is generally necessary to maintain the appropriate amount of inhibitor mixture in the

distillation apparatus by adding inhibitors during the course of the distillation process. Such addition may be carried out either on a generally continuous basis or it may consist of intermittently charging inhibitor into the distillation system in order to maintain the concentration of the inhibitor in excess of the minimum required level, or a combination
5 of these procedures may be employed.

The present invention enables the distillation and purification of olefinic compounds in manufacturing plants to operate more economically compared to prior art processes because of its greater effectiveness with or without the presence of oxygen. This permits
10 lower inhibitor usages with minimal polymer formation with accompanying economic and environmental advantages.

The present invention also enables the storage of olefinic compounds for prolonged periods of time at ambient or elevated temperatures with or without the presence of
15 oxygen by utilising economically beneficial amounts of said free radical scavenger composition to minimise polymer formation.

The present invention is illustrated, by way of example, but not in any limitative sense as follows:

20

Examples 1 to 13

Commercial quality styrene was washed with dilute caustic soda solution to remove the storage stabiliser, tert-butyl-catechol. The styrene was then washed with water to
25 remove excess alkali, following which it was dried over anhydrous sodium sulphate prior to use as follows:

Inhibitor and styrene (enough to make total weight of mixture of 200g) were charged to a 250ml round-bottomed flask fitted with an overhead stirrer, thermometer, sparge tube
30 and water cooled condenser. The stirrer was started. Nitrogen (200ml min^{-1}) sparging through the reaction mixture was applied. The reaction mixture was heated to 100°C using an oil bath, and stirred at this temperature for two hours. Samples were removed and analysed for polystyrene content using a spectrophotometric method at 420nm. The analysis method was based on American Standard Test Method D2121 and a calibration

was made using authentic polystyrene in styrene solutions of known concentration by weight. In a controlled experiment, without any inhibitor present much greater than 30000 ppm (limit of quantification) of polystyrene was formed.

This procedure was repeated as Examples 1 to 13 which differ in the addition to the
5 styrene of various Components according to the present invention (See Table 1). The results of the polymer content measurements show that combinations of Components were effective in reducing the amount of polymer formed whereas the components when used individually were ineffective. These results demonstrate that a true inhibitor effect occurs in the polymerisation inhibition of styrene in the absence of air by using a
10 reducing agent (Component 1) in the presence of a metal containing compound (Component 2) and an optional proton acid compound (Component 3).

Table 1: Polymerisation Control in Styrene under Nitrogen at 100°C

Example No	Component 1 (ppm)	Component 2 (ppm)	Component 3 (ppm)	Polymer (ppm)
Control 1				
1				30,000 @ 2 hrs
2			C ₈ /C ₁₀ Acid fatty (700)	50, 000 @ 2 hrs
3			Trifluoroacetic acid(700)	58,000 @ 2 hrs
4			Phenol (700)	45,000 @ 3 hrs
5		Ferrocene (50)		80,000 @ 2 hrs
6		Ruthenocene (50)		90,000 @ 2 hrs
7		t-Bu ferrocene (50)		80,000 @ 2 hrs
8	Phenidone B (700)			7,500 @ 4 hrs
9	Phenidone B (700)	Ferrocene (50)		0 @ 6.0 hrs
10	Phenidone B (1500)			7,000 @ 6 hrs
11	Phenidone B (1500)	Ruthenocene (50)		0 @ 7.5 hrs
12	Phenidone B (1500)	t-Bu ferrocene (50)		0 @ 7.0 hrs
13	1,8-diaminonaphthalene (700)			2,700 @ 2 hrs
	1,8-diaminonaphthalene (700)	Copper naphthenate (50)	C ₈ /C ₁₀ Acid fatty (700)	100 @ 2 hrs

Examples 14 and 15

Commercial quality methyl methacrylate was washed with dilute caustic soda to remove the storage stabiliser, hydroquinone. The methyl methacrylate was then washed with water to remove excess alkali, following which it was dried over anhydrous sodium sulphate prior to use as follows:

Inhibitor and methyl methacrylate (to a total weight of 200g) were charged to a 250ml round-bottomed flask fitted with overhead stirrer, thermometer, sparge tube and water cooled condenser. The stirrer was started. Nitrogen sparging (200ml min^{-1}) was applied to the methyl methacrylate/inhibitor and the flask contents were heated to 100°C using an oil bath. Samples were removed following 2 hours at 100°C and analysed for poly(methylmethacrylate) using gravimetry, as follows:

The test material (10mls) was added to methanol (15mls) with continuous stirring by means of magnetic follower. Following the addition the stirring was continued for 15 minutes then the mixture was filtered through a pre-dried and weighed porous glass sinter (No 3). The sinter was then dried to constant weight in a vacuum oven at $50^{\circ}\text{C}/500\text{mmHg}$. The results are shown in Table 2 (below).

Table 2

Example	Component 1 ppm	Component 2 ppm	Component 3 ppm	Polymer @ 2 hrs ppm
Control 2	-	-	-	7500
14	Phenidone A 0.01 ppm	-	-	3200
15	Phenidone A 0.01 ppm	Ferrocene 0.001 ppm	-	0 (2.5 hrs)

Examples 16-18

Commercial quality styrene was prepared as per Examples 1 to 13. Inhibitor and styrene mixture was charged to a round bottomed flask fitted with an overhead stirrer, thermometer, sparge tube and water cooled condenser. The flask was constructed with an

overflow arm which allowed a constant level to be maintained when fresh inhibitor and styrene mixture was fed into the flask on a continuous basis. The rate of continuous feed to the flask was such that its contained volume was fed over two hours (dwell time). The stirrer was started. Nitrogen sparging was applied through the flask contents and through a reservoir of inhibitor and styrene mixture used for the continuous feed. The flask contents were heated to 115°C using an oil bath and held at this temperature during the test period when the continuous feed was supplied to the flask. Samples were removed and analysed for polystyrene content as per Examples 1 to 13. It was found that after a period amounting to 2-3 times the dwell time a steady state concentration of polymer was obtained in the flask contents. The polymer so obtained at steady state was determined using the method as in Examples 1 to 13.

This procedure was carried out with styrene containing inhibitor comprising 100ppm (based on the styrene) of 2,2,6,6-tetramethyl-4-hydroxy piperidine-N-hydroxyl (4-HTOH) and various amounts of ferrocene. Results are tabulated in Table 3, below.

Table 3

Example	Component 1	Component 2	Polymer at steady state
16	4-HTOH 100ppm	-	11,000 ppm
17	4-HTOH 100ppm	Ferrocene 5ppm	750 ppm
18	4-HTOH 100ppm	Ferrocene 25ppm	988ppm

The results in Table 3 were obtained under continuous operating conditions. Under such conditions a true inhibitor is consumed. A continuous feed of fresh inhibitor ensures that a dynamic equilibrium is established with a steady state concentration of polymer being observed. The results in Table 3 are therefore further evidence that a true inhibitor effect occurs in the polymerisation inhibition of styrene in the absence of air by using a reducing agent (Component 1) in the presence of a metal containing compound (Component 2).

Claims

1. A composition comprising:
an effective amount sufficient to inhibit polymerisation of an ethylenically
5 unsaturated monomer or mixture of monomers polymerisable by free radical
polymerisation of at least one compound which is capable of acting as a reducing
agent ("Component 1") and at least one metal-containing compound where the
metal is capable of existing in an ionic form with at least two different oxidation
states ("Component 2") and optionally at least one compound capable of acting as a
10 proton acid ("Component 3"), said composition comprising
 - (i) 30 to 99.9% by weight of Component 1 based on the total weight of
Components 1 and 2 and 3;
 - (ii) 0.1 to 25% by weight of Component 2 based on the total weight of
Components 1 and 2 and 3; and
 - 15 (iii) 0 to 69.9% by weight of Component 3 based on the total weight of
Components 1 and 2 and 3.
2. A composition according to Claim 1 wherein compounds of said Component 1 are
selected from the group comprising organic compounds characterised in that they
20 possess an electrode potential relative to the standard silver/silver chloride
electrode in acetonitrile in the range 0.00V to +1.2V and preferably in the range
0.50V to +0.9V.
3. A composition according to Claim 1 or 2 wherein Component 1 comprises one or
25 more hydroxylamine compounds.
4. A composition according to Claim 1 or 2 wherein Component 1 comprises a
cycloaliphatic hydroxylamine.
- 30 5. A composition according to Claim 1 or 2 wherein Component 1 comprises an N-
hydroxypiperidine.

6. A composition according to Claim 1 or 2 wherein Component 1 comprises 2,2,6,6-tetramethyl-4-hydroxypiperidine-N-hydroxyl.
7. A composition according to any of Claims 1 to 6 wherein compounds of said Component 2 are selected from the group comprising metal containing compounds which are soluble in or miscible with the material to be stabilised.
8. A composition according to Claim 7 wherein Component 2 comprises an organometallic compound.
9. A composition according to claim 7 wherein Component 2 comprises ferrocene.
10. A composition according to any of Claims 1 to 9 wherein compounds of said Component 3 are selected from the group comprising organic acids preferably with a pKa in the range 0.5 to 12 which group includes optionally substituted aliphatic branched or straight chain carboxylic acids containing up to 22 atoms, aromatic carboxylic acids and heterocyclic carboxylic acids, optionally substituted phenols and alcohols.
11. A composition according to Claim 1 wherein said compound which is capable of acting as a reducing agent is the same compound as said metal-containing compound.
12. A composition according to Claim 1 wherein said compound which is capable of acting as a reducing agent is the same compound as said compound capable of acting as a proton acid.
13. A composition according to Claim 1 wherein said metal-containing compound is the same compound as said compound capable of acting as a proton acid.
14. A composition according to Claim 1 wherein said compound which is capable of acting as a reducing agent, said metal-containing compound and said compound capable of acting as a proton acid are the same compound.

15. A composition according to any preceding Claim further comprising an ethylenically unsaturated monomer or mixture of monomers polymerisable by free radical polymerisation, said composition being stabilised against premature polymerisation.
- 5
16. A process for inhibiting polymerisation of an olefinic compound during distillation or purification or storage which comprises incorporating therein a composition as set out in any one of claims 1 to 14 in an effective amount sufficient to inhibit polymerisation during distillation or purification or storage of said olefinic compound.
- 10
17. Use of a composition as set out in any one of claims 1 to 14 as a free radical capture agent or scavenger composition.
- 15
18. Use according to claim 17 for inhibiting polymerisation of an olefinic compound during distillation or purification or storage.

INTERNATIONAL SEARCH REPORT

International Classification No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K15/02 C07C7/20 C07B63/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K C07C C07B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 25872 A (SCHROEDER JUERGEN ; SUTORIS HEINZ FRIEDRICH (DE); BASF AG (DE); KES) 18 June 1998 (1998-06-18) claims 1,8,9	1-18
X	<p>-----</p> <p>CHEMICAL ABSTRACTS, vol. 80, no. 20, 20 May 1974 (1974-05-20) Columbus, Ohio, US; abstract no. 109575, KORSHAK, V. V. ET AL: "Stabilization of chloroprene" XP002121594 abstract & SU 396 310 T (KORSHAK, V. V.; DZHASHI, L. V.; SOSIN, S. L.; ANTIPOVA, B. A.; KARAPETY) 29 August 1973 (1973-08-29)</p> <p>-----</p> <p style="text-align: center;">-/--</p>	1,2,7-9, 11,18

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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